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AMENDED SPECIFICATION

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PATENT SPECIFICATION



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COMPLETE SPECIFICATION

Improvements in or relating to the Production of Formic Acid

We, E. I. DU PONT DE NEMOURS AND Co., of Wilmington, Delaware, United States of America, a Company registered under the laws of the State of Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the catalytic production of formic acid by the reaction of carbon monoxide with steam, and particularly to improved catalysts for the purpose of this reaction.

It is well known that carbon monoxide and steam will react, in the presence of a suitable catalyst to give formic acid, and as this process is one which employs raw materials that are relatively inexpensive, it should, under favourable conditions, produce formic acid at an exceptionally low cost. Its commercial success, however, will in no small part be determined by the catalyst used. Efforts of investigators in this art have been directed, therefore, to the discovery of catalysts having high activity and which, furthermore, favour the production of formic acid while tending to inhibit the formation of undesirable side products.

According to the present invention, formic acid is prepared from carbon monoxide and steam by passing a mixture of these gases over a non-volatile catalyst which comprises an acid salt derived from an acidic oxide of phosphorus, arsenic, tungsten, molybdenum, uranium, chromium, vanadium, titanium, boron, silicon and zirconium. Thus we may use primary

or secondary phosphates of zinc, calcium, magnesium, sodium, potassium, copper, cerium, or thorium; or the acid salts formed between these metals and the oxides of tungsten or molybdenum. We may also use non-volatile catalysts comprising two or more of the above-specified acidic oxides mutually combined, such as phospho-molybdic acid, phospho-tungsten acid, phospho-silicic acid, chromium vanadate, vanadium molybdate, silico-tungstic acid of silico-molybdic acid. These catalysts may be used alone or as admixtures and may be either unsupported or supported upon the usual type of catalyst support such, for example, as activated charcoal, Fuller's earth and kieselguhr.

The carbon monoxide required for the reaction may be derived from various commercial sources, such as, for example, water-gas or producer gas, by liquefaction or other methods, and should for the best results be as pure as possible. Inert gases, such as nitrogen or carbon dioxide, may be included with the reactants, this being advantageous in some cases from the standpoint of controlling the temperature.

We prefer to conduct the reaction at pressures in excess of atmospheric, say from 25—900 atmospheres. The reaction proceeds over a wide range of temperatures employing the above described catalysts, depending upon the gaseous mixtures employed. Generally the desired conversion of the carbon monoxide and steam to formic acid can be obtained at a temperature of from 100—400° C. although we prefer to conduct the reaction in the range of from 200—300° C.

The apparatus which may be employed

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for conducting the reaction may be of any convenient type and preferably one in which the temperature of exothermic reactions can be readily controlled at the desired temperature. Owing to the corrosive action of formic acid, the interior of the converter and conduits therefrom should preferably be protected. This may be accomplished by using glass or glass-lined apparatus or by coating the inner surfaces of the apparatus with chromium or silver or using for the construction of this equipment acid-resisting alloys of, for example, molybdenum, cobalt, tungsten, chromium, manganese or nickel.

The following examples will illustrate methods of practicing the invention, although the invention is not limited thereto.

EXAMPLE 1.

A gaseous mixture consisting of 90 parts by volume of carbon monoxide, and 20 parts by volume of steam is passed at a pressure of 700 atmospheres and a temperature of 325° C. over an acid zinc phosphate catalyst. This catalyst may be prepared by adding to an aqueous phosphoric acid solution a suitable amount of zinc oxide and subsequently impregnating a support, such as activated charcoal, with this solution. After drying the catalyst at approximately 120° C. it is ready for use. Upon condensation of the reaction product a condensate will be obtained containing formic acid.

EXAMPLE 2.

A gaseous mixture comprising 95 parts by volume of carbon monoxide and 20 parts by volume of steam is passed over a primary calcium phosphate catalyst at a pressure of 200 atmospheres and a temperature of approximately 325° C. A good yield of formic acid admixed with other aliphatic carboxylic acids will be obtained.

EXAMPLE 3.

A gaseous mixture consisting of 90 parts by volume of carbon monoxide, and 20 parts by volume of steam was passed at a pressure of 700 atmospheres and a temperature of 325° C. over a silico-tungstic acid catalyst. This catalyst was prepared by mixing a solution of sodium silicate with a solution of sodium tungstate containing an equivalent amount of sodium tungstate. The resulting solution was acidified with hydrochloric acid and extracted with ether. The ether was evaporated from the extract and the residue taken up with water, the aqueous solution of the residue being used to impregnate silica gel. This catalyst was disposed in a suitable type of reaction chamber for conducting exothermic

gaseous reactions. Upon condensation of the reaction product, a condensate containing a high percentage of formic acid was obtained.

EXAMPLE 4.

A gaseous mixture comprising 95 parts by volume of carbon monoxide and 20 parts by volume of steam was passed over a silico-molybdic acid catalyst. The pressure during the reaction is maintained at approximately 200 atmospheres and the temperature at approximately 325° C. A good yield of formic acid admixed with other aliphatic carboxylic acids will be obtained.

We do not claim the use of catalysts containing substantial quantities of iron, nickel or cobalt, or their compounds.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that, subject to the preceding disclaimer, what we claim is:—

1. A process for the production of formic acid which comprises passing a mixture of carbon monoxide and steam over a non-volatile catalyst comprising an acid salt derived from an acidic oxide of phosphorus, arsenic, tungsten, molybdenum, uranium, chromium vanadium, titanium, boron, silicon, or zirconium.

2. A process as claimed in claim 1, in which the acid salt is a primary or secondary phosphate of zinc, calcium, magnesium, sodium, potassium, copper, cerium, or thorium, or the acid salts formed between these metals and the oxides of tungsten or molybdenum.

3. A process for the production of formic acid which comprises passing a mixture of carbon monoxide and steam over a non-volatile catalyst comprising two or more mutually combined acidic oxides of phosphorus, arsenic, tungsten, molybdenum, uranium, chromium, vanadium, titanium, boron, silicon or zirconium.

4. A process as claimed in claim 3, in which the catalyst comprises phosphomolybdic acid, phospho-tungstic acid, phospho-silicic acid, chromium vanadate, vanadium molybdate, silico-tungstic acid, or silico-molybdic acid.

5. A process as claimed in claim 1, 2, 3 or 4, in which the reaction temperature is 100—400° C., preferably 200—300° C.

6. A process as claimed in claim 1, 2, 3, 4 or 5, in which the reaction is effected under pressure, e.g. 25—900 atmospheres.

7. A process for the production of formic acid, substantially as hereinbefore described.

8. Formic acid, whenever prepared by the process claimed in any of claims 1—7.

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